Photo-induced Isomerization and Polymerization of (Z,Z)-Muconate Anion in the Gallery Space of [LiAl$_2$(OH)$_6$]$^+$ Layers

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Photoreaction of guest organic anions in layered organic-inorganic hybrid materials was investigated. The layered hybrids were synthesized by an anion-exchange reaction of [LiAl$_2$(OH)$_6$]Cl·yH$_2$O layered double hydroxide with aqueous (Z,Z)- and (E,E)-muconates under inert atmospheric condition, to give new organic-inorganic hybrids of [LiAl$_2$(OH)$_6$]$_2$[(Z,Z)-C$_6$H$_4$O$_4$]·zH$_2$O and [LiAl$_2$(OH)$_6$]$_2$[(E,E)-C$_6$H$_4$O$_4$]·zH$_2$O, respectively. The basal spacings calculated by XRPD of intercalates indicate that muconate anions have almost vertical arrangements against the host [LiAl$_2$(OH)$_6$]$^+$ lattices in the interlayer of organic-inorganic hybrid materials. When UV light was irradiated on the suspension of [LiAl$_2$(OH)$_6$]$_2$[(Z,Z)-C$_6$H$_4$O$_4$]·zH$_2$O, the (Z,Z)-muconate anions of the gallery space of hybrids were polymerized in the aqueous media while it was isomerized into more stable (E,E)-muconate in the methanollic suspension in the presence of catalytic amount of molecular iodine. All the products were characterized using elemental analysis, TGA, XRPD, FT-IR, ^{1}H NMR and ^{13}C CP-MAS NMR.

Keywords : Muconates, LDH, Photoreactions, Isomerization, Polymerization.

Introduction

Host-guest chemistry involving layered materials has received considerable attention because of their structural stability, homogeneity of basic structure, tunability of chemical compositions, possibility of intercalation of the special molecules or ions into the interlayer and production of unique sites for chemical reactions.[1] Synthetic layered double hydroxides (LDHs) are a family of layered materials[2] and are able to intercalate inorganic, organic or biomolecular guest anions into the interlayer space.[1a,1f,3] The LDHs are now widely studied materials due to potential applications in various research area and industrial purposes such as catalysts, catalyst precursors, anion-exchangers, medicines, polymer stabilizers, and nanometer-sized composite materials.[3,4]

Many layered hybrids intercalated with carboxylates have been reported and discussed their structure-property correlations.[5] Application areas for such hybrid materials have expanded from their original base of enhanced mechanical properties to novel materials for separation, electro and magnetic switch and catalytic processes. Muconic acid, 2,4-hexadienedioic acid, is one of the π-conjugated dicarboxylic acids having two double bonds at 2- and 4-positions. Muconate can exist as three geometric isomers: (Z,Z)-, (E,Z)-, and (E,E)-forms. Through thermodynamic and/or photo-induced processes, less stable (Z,Z)-muconate may convert to one of other isomers.[6] Such isomerization could occur in the gallery space of layered organic-inorganic hybrid materials. These conformational changes result not only in a change of geometry, orientation and dipole moment of guest anions but also in a change in physical properties of hybrids such as

interlayer spacing, and thermal, mechanical, optical and magnetic properties.

Also, muconate is considered as one of 1,3-diene derivatives, it can polymerize via group transfer reaction by radical initiator or photoirradiation.[7] Some polymer-inorganic hybrid materials involving LDHs have been reported.[5c,5f] Polymerization of π-conjugated dicarboxylate in the gallery space of LDH gives a polymer-inorganic hybrid materials, and results in the enhancement of mechanical strength and thermal stability.

In this paper, we describe the preparation of new organic-inorganic hybrid LDHs by the anion-exchange reactions of aqueous (Z,Z)- and (E,E)-dibenzylammonium muconates with [LiAl$_2$(OH)$_6$]Cl·yH$_2$O. We discuss the photochemical reactions of (Z,Z)-muconate in the gallery space of [LiAl$_2$(OH)$_6$]$^+$ lattices under various reaction conditions involving the chemical and structural properties of hybrids, investigated by the elemental analysis, X-ray powder diffraction, FT-IR spectroscopy, thermal analysis, and ^{1}H NMR and ^{13}C CP-MAS NMR spectroscopy.

Experimental Sections

Synthesis. All chemicals were of reagent grade and were used as received without further purification. Deionized (DI) water was used for the reaction after decarbonation, which was achieved by boiling under argon atmosphere for 1 h. (Z,Z)-, and (E,E)-Dibenzylammonium muconates were prepared by the method described in the literature.[7e] All the reactions of CO$_2$ sensitive materials were performed in Schlenk ware under purified argon atmosphere in order to avoid a contamination of carbonate from air. Photoirradiation of [LiAl$_2$(OH)$_6$]$_2$[(Z,Z)-C$_6$H$_4$O$_4$]·zH$_2$O and [LiAl$_2$(OH)$_6$]$_2$[(E,E)-C$_6$H$_4$O$_4$]·zH$_2$O was carried out using a high-

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pressure mercury lamp (400 W and 313, 366, 405 and 435 nm) at a distance of 25 cm through a Pyrex filter under argon atmospheric conditions at room temperature. Except for photoreaction, glassware wrapped with aluminum foil was used for light sensitive (Z,Z)-muconate and the resulting solid samples were handled under 10 W red-bulb light in order to minimize the photoreaction. $[LiAl_2(OH)_6]Cl \cdot yH_2O$ was synthesized by stirring a suspension of the gibbsite in an aqueous solution containing a 4-fold molar excess of lithium chloride as similar method described by O'Hare.[8] Anion-exchange capacity (AEC) of $[LiAl_2(OH)_6]Cl \cdot yH_2O$: 3.875 meq g^{-1}. Elemental Anal. Found for $[LiAl_2(OH)_6]Cl \cdot yH_2O$: Al 25.18; Li 3.04; H 3.83; Cl 13.74. The LDHs intercalated with muconates were synthesized by the anion-exchange reaction of $[LiAl_2(OH)_6]Cl \cdot yH_2O$ (5.04 mmol) with (Z,Z)- and (E,E)-dibenzylammonium muconate (2.15 g, 6.03 mmol) in aqueous solution (50 mL) at room temperature for 2 h under argon atmosphere, filtered, washed with DI water (50 mL) and dried at room temperature. The prepared inter-calation compounds are expected to have experimental for-mulae as following, $[LiAl_2(OH)_6]_2[(Z,Z)-C_6H_4O_4] \cdot zH_2O$ (de-noted as **LDH-ZZ-MU**) and $[LiAl_2(OH)_6]_2[(E,E)-C_6H_4O_4] \cdot zH_2O$ (as **LDH-EE-MU**), respectively. Elemental Anal. Found for $[LiAl_2(OH)_6]_2[(Z,Z)-C_6H_4O_4] \cdot zH_2O$ Al 16.41; Li 1.79; C 10.83; H 5.17, and found for $[LiAl_2(OH)_6]_2[(E,E)-C_6H_4O_4] \cdot zH_2O$ Al 17.83; Li 2.07; C 10.99; H 5.42.

Photo-induced reactions of LDH-ZZ-MU. Powdered sample of LDH-ZZ-MU (0.650 g) was suspended on the 100 mL of solvent (methanol or water). The mixture was deae-rated by bubbling with argon for 30 min, and a well-dispersed colloidal suspension was obtained by ultrasoni-cation for 1 min. The suspension was irradiated with high-pressure mercury lamp with continuous stirring for 20 h at room temperature, filtered, washed with DI water and dried at room temperature. In the case of methanollic mixture, parallel reaction was repeated with a catalytic amount of molecular iodine (0.065 g, 0.26 mmol).

Deintercalation of muconate from LDH lattice. In order to more precisely determine the distribution of the each muconate anion between the LDH layers, the solid hybrids can be further treated with an excess of Na_2CO_3 in D_2O in order to exchange out the intercalated organic anions.[8a,9] Typically, 0.100 g of hybrids was mixed with 4 fold excess of Na_2CO_3 in 2 mL of D_2O and stirred at 40 °C overnight. The supernatant was separated by syringe filter and the filtrate was placed in a 5 mm ^1H NMR tube and analyzed immediately after deintercalation reaction by ^1H NMR spectroscopy.

Chemical analyses and physical techniques. The contents of C, N and H of the synthetic LDHs were analyzed using an EA 1110 elemental analyzer of CE Instrument and the contents of metals were determined by using an ICPS-1000IV analyzer of Shimadzu. The content of chloride in carbonate-extracted solution of intercalates was determined by a chloride ion-selective electrode of Istek combined electrode. X-ray powder diffraction spectra were recorded on a MAC Science 18XMF diffractometer using Cu Kα_1

radiation (1.54056 Å) with a graphite monochromater. The FT-IR spectra of the solid phases were obtained with Nicolet 205 FT-IR spectrometer on KBr pellets. Thermogravimetric analysis was carried out under air flow on a TGA 2960 of TA instrument. The ^1H NMR spectra were obtained by using a Varian 500 spectrometer at 25 °C. Chemical shifts (δ) were referenced internally using the residual signal of proton in deuterium oxide (4.82 ppm) relative to tetramethylsilane (TMS). Solid state ^{13}C NMR spectra were performed at 27 °C on a Bruker DSX 400 spectrometer operating at 100.62 MHz equipped with a cross-polarization accessory and double bearing rotor at Korea Basic Science Institute. The spectra were obtained by the cross-polarization, magic angle spinning, high-power proton dipolar decoupling (CP/MAS/DD) technique. The sample spinning frequency was 4.5 and 6.5 kHz. The spinning sidebands, which commonly occur in the spectra, were identified by comparison with two spectra obtained with different spin speed. The signal of TMS was used as an external reference for the chemical shifts.

Results and Discussion

Synthesis of LDH muconates. Treatment of $[LiAl_2(OH)_6]Cl \cdot yH_2O$ with aqueous (Z,Z)- and (E,E)-muconates solutions yields LDH-ZZ-MU and LDH-EE-MU. The data of FT-IR spectra point to the appearance of muconate anions in the products, which contains intense bands attributed to stretching vibrations of the carboxylic group, as well as intense bands that can be attributed to the stretching vibra-tions of C=C bonds of conjugated diene.[7b,7c] The characteri-stic bands in FT-IR spectra for LDHs intercalated with muconates are in the range of 1700-1200 cm^{-1}: 1590, 1559, 1546, 1406, 1355, 1319 and 1200 cm^{-1} for LDH-ZZ-MU; 1619, 1559, 1549, 1391, 1297 and 1194 cm^{-1} for LDH-EE-MU, respectively. The peak positions and relative intensities of absorption bands for different muconates make it possible to distinguish each other qualitatively.

The thermal analyses of LDHs intercalated with muconates show three regions of mass loss similar to other LDHs intercalated with dicarboxylates.[5b] The first, corresponding to the removal of physisorbed and interlayer water, is present for both samples and extends from room temperature to approximately 180 °C. The second follows the dehydroxyl-ation of the host LDH lattice in the 180-450 °C range. The third loss, above 450 °C, corresponds to the elimination and combustion of the interlayer muconates.

The solution ^1H NMR spectra for the muconates deinter-calated from LDHs muconate samples are shown in Figure 1 (a) and (b). In ^1H NMR spectra two types of *CH* protons exist in each muconate, and the chemical shifts appear at δ 5.96 and 6.94 ppm for (Z,Z)-muconate and δ 6.18 and 7.02 ppm for (E,E)-muconate as multiplets, respectively.[7e] Such differences in the chemical shifts are enough to distinguish from each other in the spectra of mixed muconates and there was no isomeric inversion of one isomer to the other during synthesis and analysis. The ^{13}C CP-MAS NMR spectra of LDHs intercalated with pure two muconate types are shown
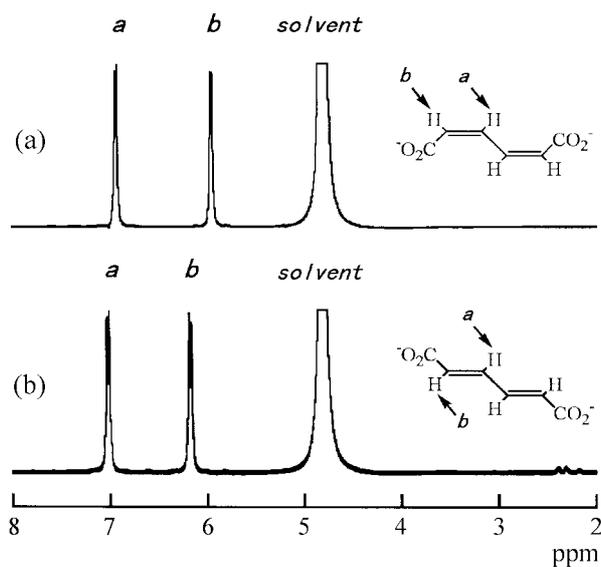
Figure 1. The ^1H NMR spectra of muconates deintercalated by aqueous carbonate from inorganic layers of (a) LDH-ZZ-MU, (b) LDH-EE-MU.

in Figure 2(a) and (b). The narrow and single peaks for each carbon observed in the spectra indicate that the muconates exist in the gallery space of hybrids without change in their original conformations during the synthesis. The very intense peaks of δ 175, 133 and 130 ppm in Figure 2(a) are assigned to the carbonyl carbons, methine carbons of 3,4-positions

and methine carbons adjacent to the carbonyl carbons of (Z,Z)-muconate, respectively.[7e] The chemical shifts of carbonyl carbons, methine carbons of 3,4-positions and methine carbons adjacent to the carbonyl carbons of (E,E)-muconate appeared at δ 174, 139 and 135 ppm, respectively as shown in Figure 2(b).[7e] These chemical shifts are close to the values for the corresponding carbons of dibenzylammonium muconates in NMR solvent revealing that the nuclear magnetic environment of each muconate in the interlayer of LDHs seems to be similar to that of the solution.

Structural studies of LDH-muconates. The X-ray powder diffraction spectra of [LiAl$_2$(OH)$_6$]Cl·yH$_2$O, LDH-ZZ-MU and LDH-EE-MU are shown in Figure 3. The measured interlayer spacing of pristine [LiAl$_2$(OH)$_6$]Cl·yH$_2$O is 7.68 Å, which is good agreement with the values reported in the literatures.[8b,10] The low intense peak at 4.84 Å ($2\theta = 18.32°$) corresponds to a residual amount of unreacted γ-Al(OH)$_3$. Any contamination by carbonate from air is not observed in the XRPD spectra of the prepared [LiAl$_2$(OH)$_6$]Cl·yH$_2$O. The observed basal spacings of wet samples of LDH-ZZ-MU and LDH-EE-MU are 13.07 and 14.06 Å, respectively. Wet samples refer to LDH intercalates materials dispersing in degassed DI water for 24 h.

The schematic diagrams of intercalates are represented in


Figure 2. The ^{13}C CP-MAS NMR spectra of (a) LDH-ZZ-MU, (b) LDH-EE-MU, and (e) photoirradiated LDH-ZZ-MU in the aqueous suspension. s: spinning side band.
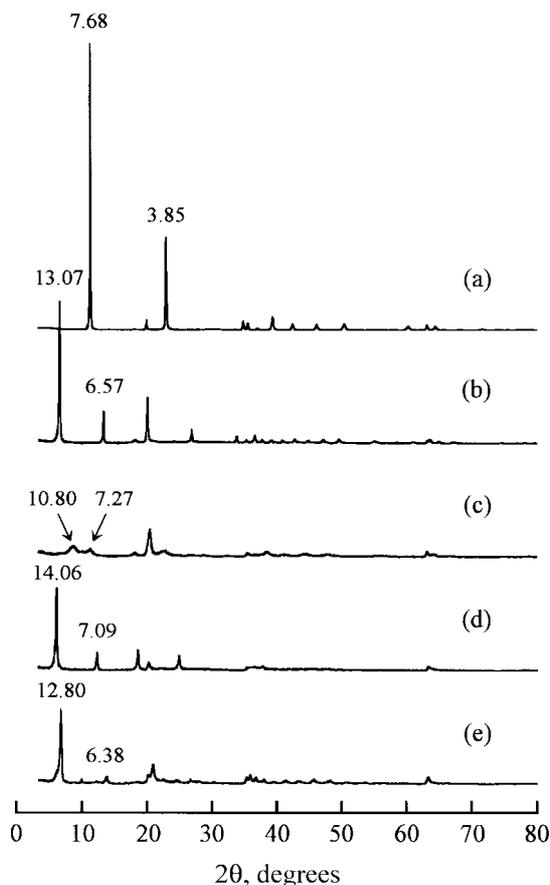
Figure 3. The X-ray powder diffraction spectra of (a) [LiAl$_2$-(OH)$_6$]Cl·yH$_2$O, (b) wet LDH-ZZ-MU, (c) dried LDH-ZZ-MU, (d) wet LDH-EE-MU, and (e) dried LDH-EE-MU. The *d*-spacings are presented in Å.

Figure 4. Intercalation of large organic anions leads to the increase of the distance of the interlayer space (d_{IL}), that is the expansion of inorganic layers along the stacking direc-

tion (c-axis). When the layer thickness ($d_{LT} = 2.10$ Å) of $[LiAl_2(OH)_6]^+$ lattices and the hydrogen bond distances ($d_{HB} = 2.70 \pm 0.1$ Å) between guest and host are subtracted from the basal spacing,[11] the distance of the interlayer space available for the anions could be calculated as values of d_{IL}, 5.57 ± 0.1 and 6.56 ± 0.1 Å for LDH-ZZ-MU and LDH-EE-MU, respectively. Compared with the dimensions of each muconate (6.21 Å for (Z,Z)-form and 7.52 Å for (E,E)-form, respectively[12]), it is suggested that the muconates in the interlayer of LDHs have almost vertical arrangements against inorganic $[LiAl_2(OH)_6]^+$ lattices. The amount of water in the interlayer space of intercalates is variable depending on the drying conditions, and the obtained intercalation compound can be described by the formula $[LiAl_2(OH)_6]_2[C_6H_4O_4]$ $\cdot z H_2O$.
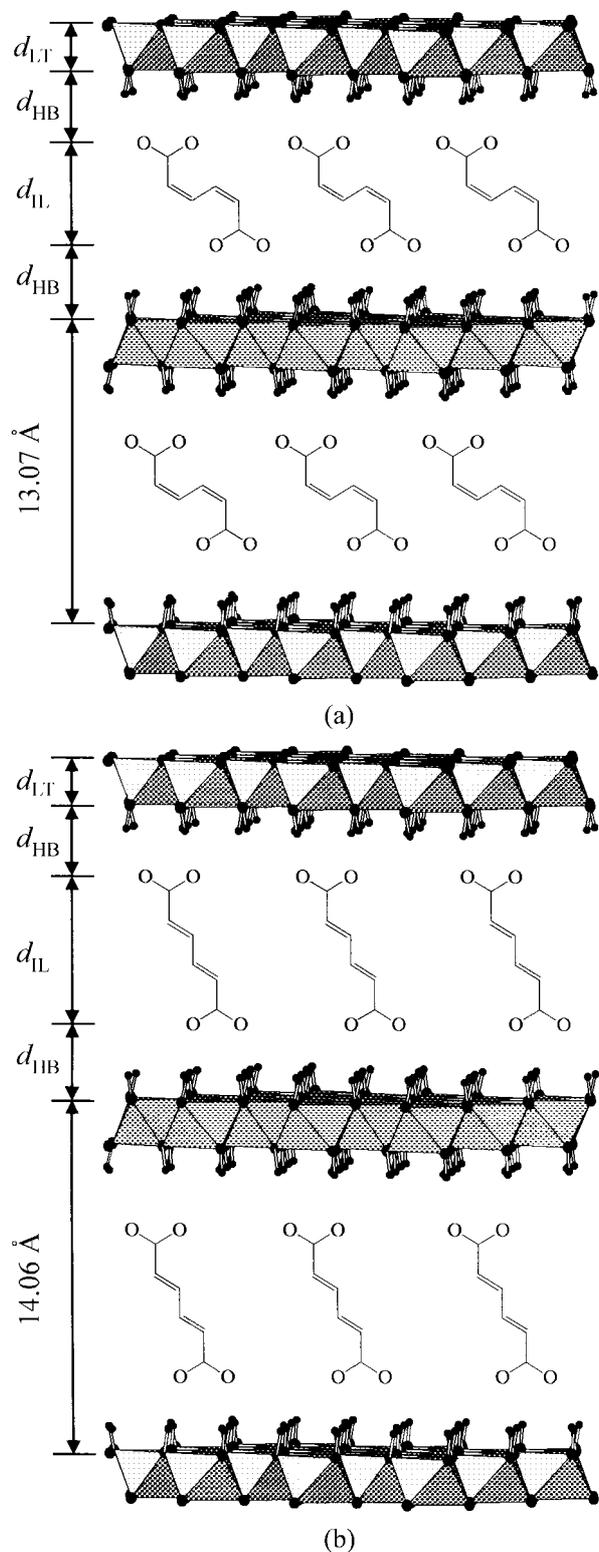
It should be noted that the basal spacing of LDH-EE-MU dried in a desiccator filled with molecular sieve at room temperature presents the value of 12.80 Å smaller than that of wet intercalate (14.06 Å) (Figure 3(e)). Desorption of the excess water during drying decreases the interlayer spacing by 1.26 Å, and slight tilting of (E,E)-muconate in the interlayer is expected to bring this change. The intensity of the (001) reflections of LDH-ZZ-MU is strongly reduced (Figure 3(c)), the shape of the peaks becomes very complex as demonstrated by the shift of $d_{(001)}$ from 13.07 to 10.80 and 7.27 Å. The value of 10.80 Å has been rationalized in terms of an ordered interstratification of collapsed and expanded layers with d value of the (002) peak close to the half of the sum of the d_{001} of the vertical orientation structure and the d_{001} of the horizontal arrangement.[5b] Metastable intermediate phases may be formed during the dehydration step. The

Figure 4. Schematic diagrams for the intercalates with muconates for (a) LDH-ZZ-MU, and (b) LDH-EE-MU. d_{LT}: layer thickness of 2.10 Å; d_{HB}: hydrogen-bond distance of 2.70 ± 0.1 Å; d_{IL}: distance of the interlayer space. Water molecules are omitted for clarity.
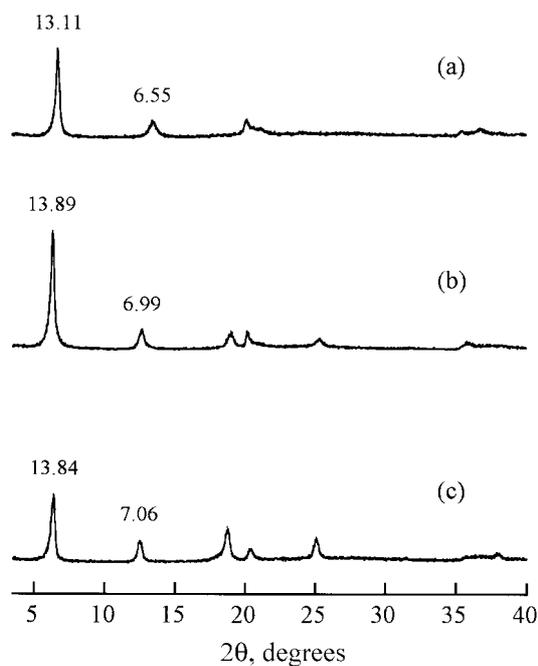
Figure 5. The X-ray powder diffraction spectra of LDH-ZZ-MU (a) photoirradiated in the aqueous suspension, (b) photoirradiated in the methanollic suspension, (c) photoirradiated in the methanollic suspension containing I_2. The d-spacings are represented in Å.
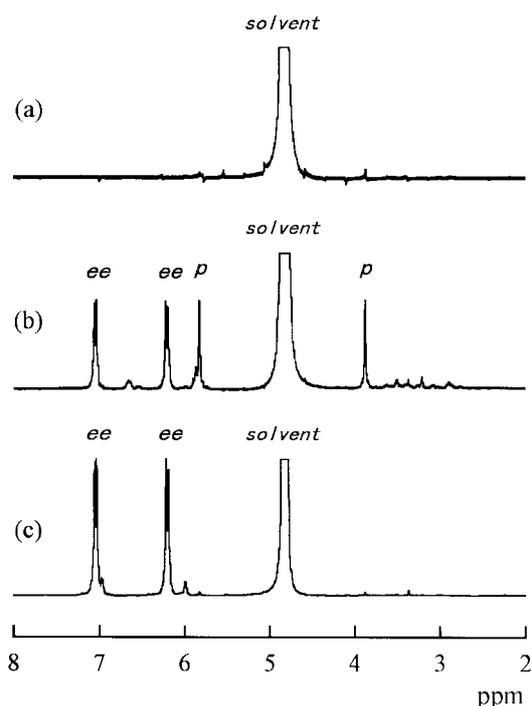
Figure 6. The ^{1}H NMR spectra of muconates deintercalated by aqueous carbonate from LDH-ZZ-MU (a) photoirradiated in the aqueous suspension, (b) photoirradiated in the methanollic suspension, (c) photoirradiated in the methanollic suspension containing I₂. *zz*: (Z,Z)-muconate, *ee*: (E,E)-muconate *p*: polymuconate.

XRPD patterns for the samples after rehydration are consistent with initial wet samples indicating that the reaction to form metastable phases is completely reversible.[5b]

Photoreaction of LDH-ZZ-MU on the aqueous suspension. The polymerization of (Z,Z)-muconate was confirmed by ^{13}C CP-MAS NMR spectra of solid phase as shown in Figure 2(c). The solid ^{13}C NMR spectra of the photoirradiated LDH-ZZ-MU gave very sharp and intense peak of the carbonyl carbons at 181 ppm shifted from 175 ppm, the signal of methine carbons on the double bond appeared at δ 131 ppm instead of 133 ppm, and the peak of methine carbons adjacent to the carbonyl carbon shifted from 130 ppm to intense 57.0 ppm and medium 51.2 ppm. These results from the condensation of (Z,Z)-muconate by photoirradiation and the double bonds of methine carbons adjacent to the carbonyl carbons are reduced to single bonds *via* a radical chain reaction.[7b] The (Z,Z)-muconates have vertical arrangement against inorganic [LiAl₂(OH)₆]⁺ lattices and are mobile in the interlayer region of LDHs. The 1,3-diene moieties are arranged in a face-to-face manner with a suitable orientation and distance for the propagation of radicals induced by photoirradiation. The methine carbons adjacent to the carbonyl carbons show a well-split pattern where the peaks at 57.0 ppm and 51.2 ppm are assigned to the *trans*-1,4- and *cis*-1,4-units of polymuconate, respectively, according to the assignments for the polymer which was prepared through group transfer polymerization by others.[7a]

The XRPD spectra of photoirradiated LDH-ZZ-MU show the small change of basal spacing (13.11 Å) as shown in Figure 5(a). However, the crystallinity becomes poorer than original sample and some reflections in the region of higher angles disappeared, implying the possibility of modification or disorder of guest anions in the interlayer of hybrids. As shown in Figure 6(a), there is no peak observed in the ^{1}H NMR spectra for the solution prepared through deintercalation by carbonate, which is ascribed to the photopolymerization of (Z,Z)-muconate[7b-7e] in the gallery space of LDH. Polymuconate may have large molecular weight and show the stronger preferential affinity for the interlayers of LDH than carbonate.

Photoreaction of LDH-ZZ-MU on the methanollic suspension. The muconate derivatives were extracted by aqueous carbonate anion and peaks of δ 6.18 and 7.02 ppm were observed in ^{1}H NMR spectra as shown in Figure 6(b). They were assigned to the protons of methine on the conjugated double bond of (E,E)-muconate formed by photoisomerization of (Z,Z)-muconate.[6,7c,7e,13] New peaks are observed at δ 5.82 and 3.87 ppm, and they could be assigned to the protons of methine on the double bond of polymuconate and the protons of methine on the adjacent to the carbonyl carbon, respectively. The degree of polymerization is relatively low and the oligomeric polymuconate ions are expected to form along with LDH-EE-MU through isomerization reaction.

In the XRPD spectra of photoirradiated sample on the methanollic suspension of the LDH-ZZ-MU the basal spacing changed from 13.07 to 13.89 Å, implying the conformational change from (Z,Z)- to (E,E)-muconates. The (E,E)-muconate do not undergo the polymerization by photoirradiation on the suspension of the LDH-EE-MU under present conditions. Therefore, photo-induced isomerization and polymerization of (Z,Z)-muconate are competitive each other in the methanollic suspension. Selective photoisomerization of (Z,Z)-muconate into more stable (E,E)-muconate was achieved by addition of catalytic amount of molecular iodine. XRPD and ^{1}H NMR spectra show that only selective isomerization reaction occurred to give an LDH-EE-MU. Though small quantity of LDH-ZZ-MU remains without change, there is no evidence for the photopolymerization (Figure 5(c) and Figure 6(c), respectively).

Inorganic [LiAl₂(OH)₆]⁺ lattice offers a well-oriented reaction site for the photoreaction of guest organic anion. Charge density of inorganic [LiAl₂(OH)₆]⁺ lattice and dimension of guest organic anion make it possible to arrange the (Z,Z)-muconate with a proper orientation in the gallery space of LDH for the propagation of dienyl radicals induced by photoirradiation. This allows to form a new polymer-inorganic hybrid materials, [LiAl₂(OH)₆]₂ₙ[C₆H₄O₄]ₙ·zH₂O by *in situ* photopolymerization of guest anions. Molecular iodine plays a key role in the promoting the photoisomerization of (Z,Z)-muconate under suppression of photopolymerization. The reaction pathways of (Z,Z)-muconate in the gallery space of inorganic layers of LDH are summarized in Scheme 1.

Conclusion

The results presented here demonstrate that new layered

$$[LiAl_2(OH)_6]Cl\cdot yH_2O$$

$(Z,Z)\text{-}C_6H_4O_4{}^{2-}(aq)$ $(E,E)\text{-}C_6H_4O_4{}^{2-}(aq)$

LDH-ZZ-MU: $\xrightarrow[\text{MeOH}]{I_2, h\nu}$ LDH-EE-MU: $\xrightarrow[\substack{H_2O\ or\\MeOH}]{h\nu}$ no isomerization no polymerization

$h\nu$ | H_2O $\underset{MeOH}{h\nu}$

LDH-poly-MU: LDH-EE-MU:
                                        +
                                     LDH-poly-MU:

LDH-ZZ-MU: $[LiAl_2(OH)_6]_2[(Z,Z)\text{-}C_6H_4O_4]\cdot zH_2O$

LDH-EE-MU: $[LiAl_2(OH)_6]_2[(E,E)\text{-}C_6H_4O_4]\cdot zH_2O$

LDH-poly-MU: $[LiAl_2(OH)_6]_{2n}[C_6H_4O_4]_n\cdot zH_2O$
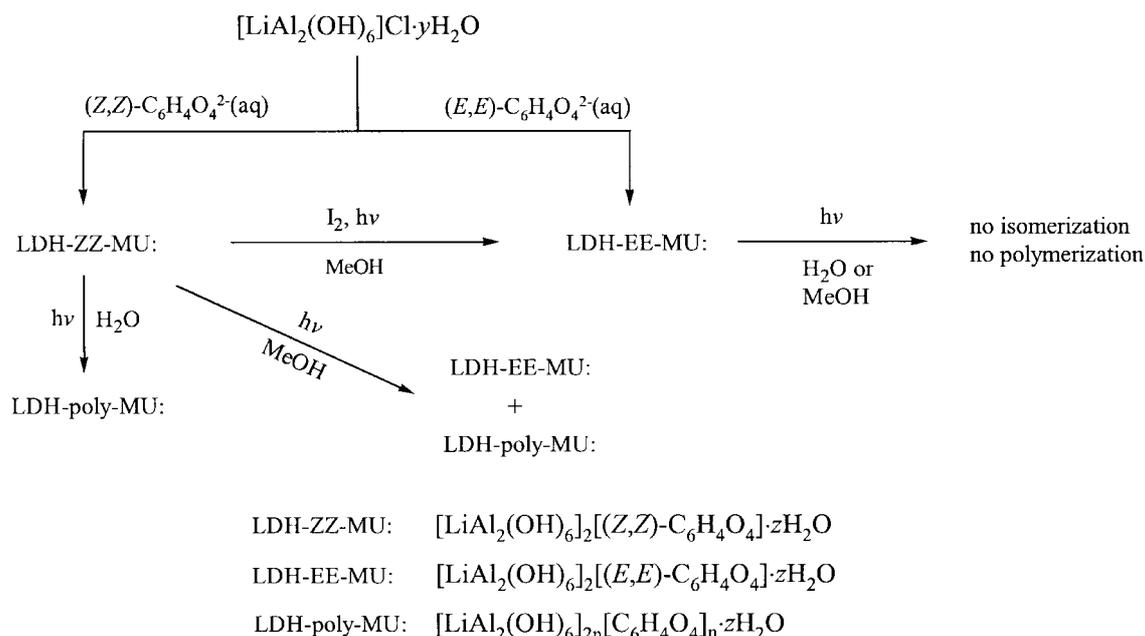
Scheme 1. The reaction pathways of (Z,Z)-muconate in the gallery space of inorganic layers.

organic-inorganic hybrid materials $[LiAl_2(OH)_6]_2[(Z,Z)$-$C_6H_4O_4]\cdot zH_2O$ and $[LiAl_2(OH)_6]_2[(E,E)$-$C_6H_4O_4]\cdot zH_2O$ could be prepared by anion-exchange reaction. Light sensitive (Z,Z)-muconate undergoes photopolymerization and photoisomerization in the gallery space of inorganic layers by irradiation of UV light. In addition, it is clear that the reaction media play a key role in determining the reaction products formed by photoirradiation to the (Z,Z)-muconate in the suspension: Polymerization is main process in the aqueous media while isomerization is preferred in the methanollic suspension containing catalytic amount of molecular iodine. Structural as well as conformational modifications in the organic-inorganic hybrid materials are applicable in the improvement of both physical and chemical properties of nano-composites.

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